

SCIENCE FOR GLASS PRODUCTION

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ON THE THEORY OF GLASS SOLIDIFICATION

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The process of glass solidification is analyzed in the context of the fundamental principles of physicochemical kinetics. The concept of the emergence of “solidification seeds”, formation of “solidification layers” and their migration into the glass volume are discussed. It is demonstrated that the level of diathermancy of tinted glasses can characterize the force of the interaction between the colorant complexes and the main silicon-oxygen elements in glass and, consequently, can influence viscosity variation in solidifying. The proposed theoretical principles agree well with experimental and industrial data.

The critical factor in molding glass articles is the glass solidification rate, which depends on the combination of viscosity variation depending on temperature and temperature variation in time. As a rule, published works on the kinetics of glass solidification describe qualitative results of experiments related to different diathermancy of glasses determined by introduction of colorants [1]. The new concept of glass solidification is based on fundamental principles of physics and chemistry of melts and solids, taking into account the vitreous state and the factors of surface and volumetric interactions in glass technology processes [2].

Cooling and solidification of a highly viscous glass melt in the formation of glass articles proceed due to a complex heat exchange with the ambient medium with participation of thermal conductance and radiation. One should bear in mind the following specifics of industrial glass molding:

- highly viscous glass melt delivered for molding is not totally homogeneous chemically, thermally, and optically;
- cooling of glass melt is nonuniform; this is especially true of processes involving molds where a highly viscous glass melt contacts a heat-removing surface at a limited number of points;
- cooling and solidification of glass melt starts from the surface and extends into the glass volume;

Taking into account the above specifics of glass melt cooling, it can be assumed that viscosity variations are likely to be fragmentary, both on the surface (fast process) and inside the volume (slow process).

The results of the study in [3] demonstrated that a granular structure is registered in glass in forming, with a “grain”

size of 4–8 μm, parallel to the mold surfaces. The cross-section of molded articles (perpendicular to the mold surfaces) has a laminar structure with layer thickness of 2–4 μm. Thus, the glass solidification process in molding can be represented in two stages:

- emergence of “solidification seeds” (local areas of glass with increased viscosity) and the formation of a “solidification layer”;
- expansion of the “solidification layer” into the volume of glass.

The formation of “solidification seeds” is governed by probabilistic processes; the theoretical principles of these processes are formulated in the works of A. N. Kolmogorov (1937), M. Avramy (1939), and B. V. Erofeev (1950). According to the basic principles of these studies, the solidification rate (viscosity variation with time) is proportional to the quantity of “solidification seeds” and the viscosity gradient:

$$\frac{d\eta}{d\tau} = KN\Delta\eta,$$

where η is viscosity; τ is time; K is the proportionality coefficient; N is the number of solidification seeds; $\Delta\eta$ is the viscosity gradient.

Taking into account the number of “solidification seeds” changing according to a power law and subsequent integration, we obtain the following equation for the solidification process:

$$\eta_{\tau} = (\eta_f - \eta_0)[1 - \exp(-k\tau^n)] + \eta_0,$$

where η_{τ} is the viscosity at the given time moment; η_0 and η_f are the initial and final viscosity values; k and n are kinetic parameters.

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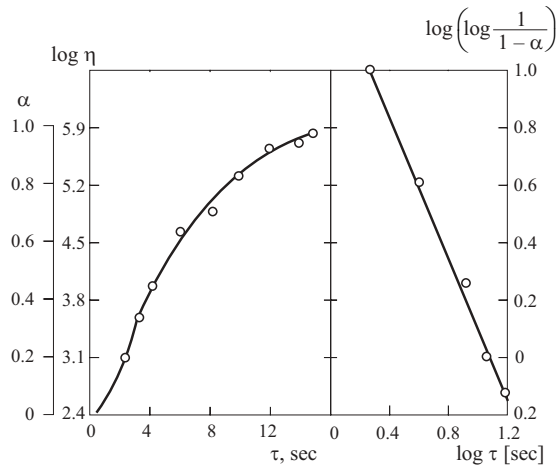


Fig. 1. Kinetics of viscosity variation at a distance of 0.15 cm from the working surface of a parison mold.

The interval of viscosity variation with time in the selected area during molding is rather wide. Therefore, it is convenient to represent viscosity variation as “the extent of transformation”:

$$\alpha = \frac{\eta_{\tau} - \eta_0}{\eta_f - \eta_0}.$$

Considering the above, we derive the following equation:

$$\alpha = 1 - \exp(-k\tau^n), \quad (1)$$

where α is the “extent of transformation” in glass solidification.

To verify the validity of the above statements and equations obtained, experiments were performed and results of a number of published studies were processed. Let us consider by way of example the process of glass viscosity variation in the “solidification layer” in molding a bottle preform using data from [4]. The viscosity is calculated based on the specified glass composition using the M. V. Okhotin method [5]. The processing of experimental data indicates that they satisfy the conditions of Eq. (1). Figure 1 shows the kinetic curve of viscosity variation and its logarithmic anamorphosis at a distance of 0.15 cm from the working surface of the parison mold. Viscosity variation can be determined for any layer of glass being cooled.

It is usually believed that glass solidification in molding occurs due to viscosity increasing in cooling up to 10^{12} Pa·sec. However glass articles in molding preserve their shape primarily due to a faster solidification of the surface layer, while the average viscosity values remain lower. Therefore, the volumetric glass solidification rate can be characterized by the velocity of propagation of a layer with viscosity 10^{12} Pa·sec into the glass melt volume or the change in the thickness of the solidified layer with viscosity 10^{12} Pa·sec or more with time. The solidification rate can

also be estimated by the changing thickness of the layer with another viscosity value within a specified time interval.

Let us analyze the process of volumetric solidification of glass depending on its cooling conditions. It is shown in [4, 6] that thermal conductance is the main factor in the cooling of thin glass layers. In this case the uniqueness of the temperature field is determined by boundary conditions, i.e., the space and time conditions differentiating the given case from other possible cases. The Newton cooling law with a certain approximation can be accepted as the spatial boundary condition. The time boundary condition determines the temperature function for the cooling glass melt volume at a given time moment.

The temperature field is described by the following equation in the criterial form:

$$\frac{t}{t_i} = f \left[\text{Bi}, \text{Fo}, \frac{x}{l} \right], \quad (2)$$

where t is the temperature at a point with the coordinate x at the given moment; t_i is the initial glass melt temperature; Bi and Fo are the Biot and Fourier numbers; $\frac{x}{l}$ is the dimensionless coordinate of the point for which the temperature is determined; l is the determining size.

Assuming as an initial approximation that the effective heat transfer coefficient and the thermal conductivity coefficient that make up part of the Biot number expression are constant within a certain temperature interval, Eq. (2) takes the following form:

$$t_1 = K_1 f_1 \left(\frac{a\tau}{l^2} \right), \quad (3)$$

where t_1 is the solidification temperature; K_1 is the proportionality coefficient; a is the temperature conductivity.

The expansion of the “solidification layer” into the glass volume is determined by the Fourier number for the heat transfer specified on the boundaries of the system considered. Therefore, assuming that τ is the time required for the solidification layer to propagate to a distance δ , the values of the criterion $a\tau/\delta^2 = a\tau/l^2$, in accordance with Eq. (3), will form a continuous series of values. For a constant a

$$a\tau = \text{Fo} \delta^2 \quad \text{or} \quad \delta = \sqrt{\frac{a\tau}{\text{Fo}}} = K_2 \sqrt{\tau} = K_2 \tau^{0.5}, \quad (4)$$

where K_2 is the proportionality coefficient.

This equation expresses the dependence of the solidified layer thickness on time. However, taking into account the assumptions made in deriving this equation, it should be written in a general form:

$$\delta = k' \tau^m \quad \text{or} \quad \log \delta = \log k' + m \log \tau, \quad (5)$$

where k' and m are coefficients.

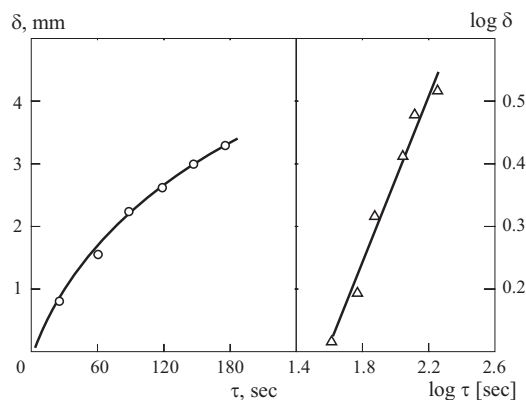


Fig. 2. Kinetic dependence of the solidified layer thickness and its logarithmic anamorphosis.

To verify the validity of Eq. (5), one of the clear glasses described in [7] was cooled in a crucible. Thermocouples were installed at different depth levels starting from the glass surface. In the course of data processing the time of reaching the temperature corresponding to viscosity 10^{12} Pa · sec was registered. The experimental results shown in Fig. 2 indicate that Eq. (5) satisfactorily describes the kinetic thickness variation of a solidified glass layer. The experimental data were used to determine the parameters of Eq. (5), which in this case takes the following form:

$$\delta = 1.65\tau^{0.661}.$$

The perceptible difference of the parameter m value from the value $m = 0.5$ in Eq. (4) is due to radiation participating in heat transfer. The results of experiments with clear and tinted glasses are represented in Fig. 3. It can be seen that the value m decreases with decreasing radiation diathermancy of glasses, approaching 0.5 in low-diathermancy glasses.

Thus, whereas inhomogeneous solidification of clear glasses is mainly caused by cooling conditions and the inhomogeneity of glass compositions, in solidification of tinted glasses there is an additional factor of heat radiation absorption.

In tinted glasses the main glass structure incorporates a relatively small number of colorant complexes interacting with thermal radiation. Glasses are most frequently tinted with transition metal compounds. According to the ligand field theory [8], the central ion of the metal reacts with surrounding ligands (for instance, oxygen ligands) arranged in a certain configuration. The following interaction forces should be considered for a colorant complex:

- internal forces (between the central ion and the ligands);
- external forces (between the colorant complex and the main structural elements of glass).

These interaction forces determine the type of radiation absorption and thus affect the glass solidification process.

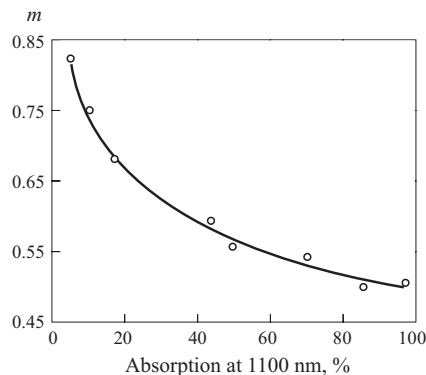


Fig. 3. Dependence of the power index m in Eq. (5) on the value of the absorption in the spectral range 1100 nm.

As a rule, trivalent transition metal ions (Ti^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+}) have a sufficiently great force field and are firmly connected with the ligands. Therefore, the colorant complexes of such metals require higher energy for splitting electron levels, as a consequence of which the absorption bands are shifted toward the short-wave spectrum range. In bivalent ions (Co^{2+} , Ni^{2+} , Fe^{2+}) the force field is lower and, accordingly, the energy of splitting electron levels is lower and the absorption bands are shifted toward the long-wave (infrared) range. This intensifies the interaction between the colorant complex and the silicon-oxygen skeleton that is the main structural element of glass. The radiation absorption and the intensified vibration energy of the silicon-oxygen skeleton decrease the viscosity and the volumetric solidification rate compared to clear glasses and glasses tinted with trivalent metal complexes. The surface layers in this case do not receive radiation energy absorbed in the volume, and therefore they cool and solidify faster. Consequently, glasses tinted with bivalent metal oxides have lower diathermancy than glasses tinted with trivalent metal oxides. Thus, for the colorant iron complexes the transition from the electron configuration d^5 (Fe^{3+}) to the d^6 (Fe^{2+}) configuration as a result of the reducing process disturbs the symmetry of the complex and weakens the bonds inside it, which strengthens the external bonds. In this case a wide absorption band emerges in the range of $1.1 \mu\text{m}$, the diathermancy becomes significantly lower, and the volumetric solidification rate decreases while the surface solidification rate grows.

It is known [9] that glass viscosity primarily depends on the state of silicon-oxygen bonds, which are responsible for viscosity variation of different glass layers in the kinetic process (in solidification). Since the content of colorant compounds in glass is relatively low and the radiation absorption is localized near the colorant complexes, the diathermancy level can characterize the force of interaction of these complexes with the main silicon-oxygen elements in glass and, consequently, can affect the variation of glass viscosity in solidifying.

The above statements agree with experimental and industrial data on the formation of a surface destruction layer

in industrial glass articles, the thermophysical properties of glasses, the molding conditions of clear and tinted bottles, and the emergence of various defects in glass article forming [10 – 12]. The data obtained can be used as a starting point in analyzing the relationship between the molding conditions and the service parameters of products, as well as in developing the general theory of molding.

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